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The dependence of the crystal structure of $YBa_2Cu_3O_{7-x}$ on the starting barium compounds

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Abstract
A comparative study of the processing of powders to obtain the high-T_c $YBa_2Cu_3O_{7-x}$ superconductor has been made. The effects of the starting barium compound and the preparation procedure on compositional homogeneity have been investigated. Our results show that the co-precipitation method using barium nitrate is a simple and convenient sintering method.

1. Introduction

$YBa_2Cu_3O_7$ compound is the most important superconducting phase of the Y–Ba–Cu–O series. It exhibits a transition temperature around 92 K and shows an ABO_3 perovskite structure [1]. Its superconductivity is sensitive to the oxygen content [2] and hence to the preparation procedure [3]. YBCO samples with good electrical and magnetic characteristics must be single-phase, homogeneous and without microstructure defects. The sample structure is strongly dependent on the synthesis conditions: starting chemical compounds and composition, sintering conditions, atmosphere of annealing, etc [4].

The most common method of preparation is the solid-state reaction method, using Y_2O_3, $BaCO_3$ and CuO as starting chemical powders. However, barium carbonate needs high decomposition temperature and in some cases small impurities of CO_2 remain in the final product [5, 6].

In our laboratory [7] YBCO samples were prepared with different starting barium precursor compounds, in order to compare their influence on the final sample characteristics. The YBCO sample preparation was performed using the usual solid-state method [8] and both the simultaneous preparation [9] and autoignition methods (via citrate solution process) [10].

2. Experimental details

Each sample was analysed with x-ray powder diffraction analysis using a D5000-Siemens diffractometer equipped with Göbel mirrors, using Ni-filtered Cu Kα radiation. The diffraction intensities in 2θ-range 20°–40° were collected in a 2θ–θ scan mode, with 0.02° steps.

Samples were also investigated with a scanning electron microscope (SEM) Oxford Instrument and the final cation stoichiometry was detected by EDX (energy dispersive x-ray) analysis. Ac-susceptibility measurements from 77 K to 95 K were performed on all samples in order to obtain the T_c value. The field was applied parallel to the large plane of the sample and its magnitude was 100 A m^{-2} at 1000 Hz. The samples were cooled to 77 K in zero magnetic field and the measurements were made increasing the temperature. The oxygen content was obtained from iodometric titration [11].

2.1. Sample preparation

Samples from six different precursors, BaO, BaO_2, $BaCO_3$, $Ba(NO_3)_2$, $Ba(CH_3COO)_2$ and $Ba(C_9H_{19}COO)_2$, were prepared using always the same stoichiometric ratios and thermal treatments. The nominal Y:Ba:Cu ratio was fixed at 1:2:3. The thermal behaviour of the used starting barium compounds is shown in table 1.

The details of sample preparation were different and related to the chosen methods (solid-state, precipitation or autoignition method). When the solid-state method [8] was used, the starting powders of Y_2O_3, CuO and of barium precursor (oxide, peroxide or carbonate) were directly ground and mixed in an agate mortar. Using the simultaneous precipitation method [9], the Y, Ba and Cu neodecanoates

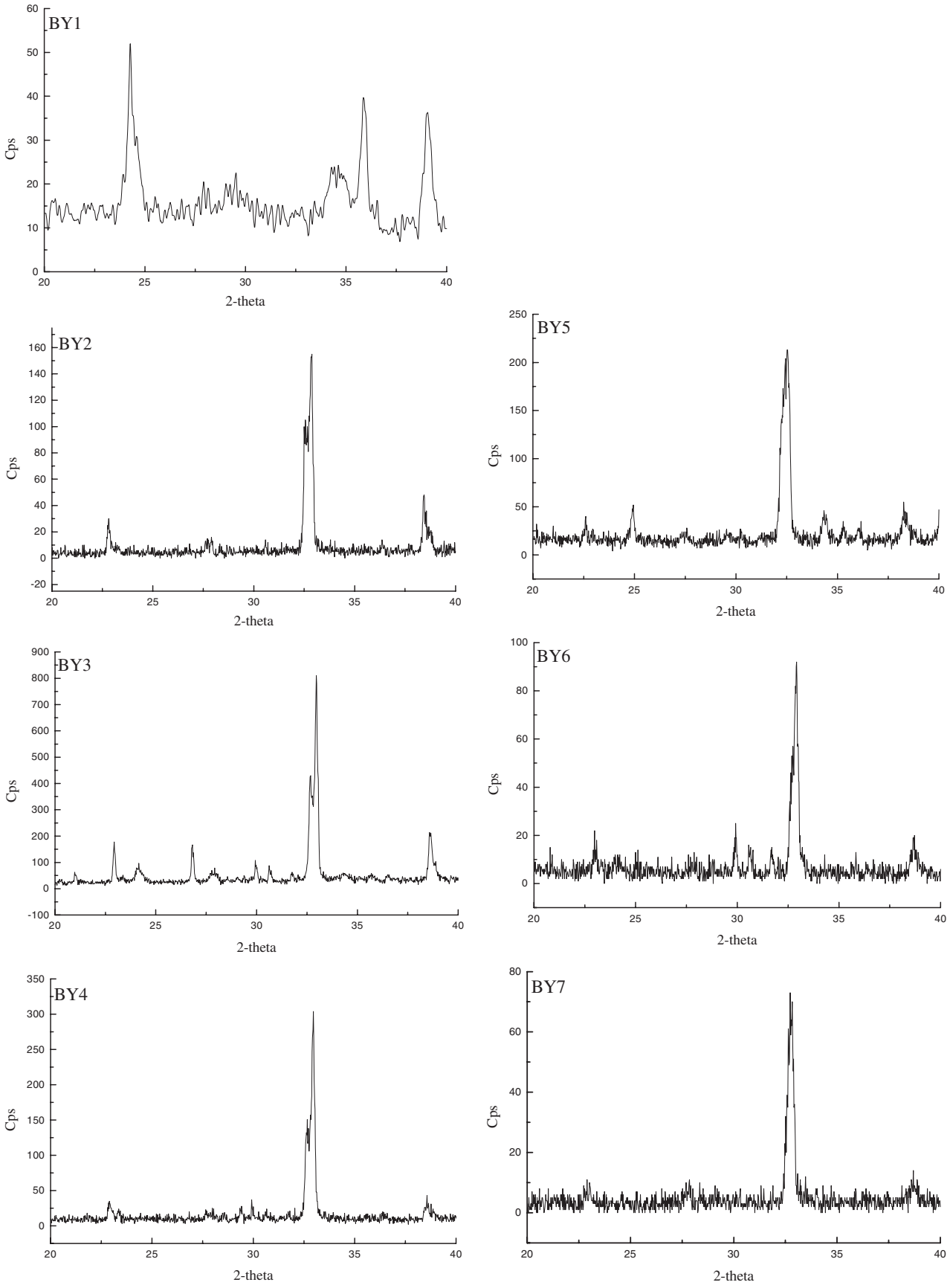


Figure 1. XRD patterns of the sample from BY1 to BY7.

Table 1. Data of barium compounds thermal behaviour [12].

Compound	Thermal behaviour
BaO	Melting point at 1918 °C
BaO_2	Melting point at 450 °C; oxygen loss at 800 °C
$BaCO_3$	Transition to β phase at 811 °C and to α phase at 982 °C; decomposition at 1450 °C
$Ba(NO_3)_2$	Melting point at 592 °C
$Ba(CH_3COO)_2$	Water loss at 150 °C
$Ba(C_9H_{19}COO)_2$	Decomposition at 300 °C

Table 2. List of the impurities present in each sample after sinterization.

Sample	Starting barium precursor	Minor phases
BY1	From oxide	$BaCuO_2$; Y_2CuO_5; CuO
BY2	From peroxide	
BY3	From carbonate	$BaCuO_2$; Y_2CuO_5
BY4	From nitrate	
BY5	From acetate	CuO; $BaCO_3$
BY6	From neodecanoate	Y-211; $BaCuO_2$
BY7	Via citrate solution	

Note: The phase impurities are listed starting from those with the highest yield.

(or nitrates or acetates) were dissolved in a xylene/pyridine mixture. The solution was then dried and calcined at 500 °C for 5 h. The powders were finally obtained by grinding and mixing. When the sample preparation was performed by the autoignition method, the Y, Ba and Cu nitrates were dissolved in an aqueous solution. The solution was stirred and heated. Then, a 3 M citric acid solution was added, causing autoignition [10].

In all cases the obtained powders were pressed at about 1 GPa and the resulting pellets underwent the same thermal treatment, consisting of two annealing steps: the first at 920 °C for 5 h and the second at 450 °C for 1 day in controlled oxygen flow. Both heating and cooling rates were of 5 °C min^{-1}.

3. Results and discussion

Figure 1 shows the diffraction patterns of samples obtained using different barium precursors but synthesized under identical conditions of sintering. The compound identification was effected comparing the peaks' positions and their relative intensities with the published crystal structure data [13].

All XRD patterns of the sample from BY2 to BY7 show the signals at $2\theta = 22.8$, 32.5, 32.8, 38.5 attributable to the YBCO-123 phase. In the sample obtained from peroxide, nitrate or via citrate solution (BY2, BY4 and BY7), Y-123 is the only phase detected, whereas the spectra of the samples obtained from carbonate, citrate or neodecanoate (BY3, BY5 and BY6) also show signals attributable to impurities, even if Y-123 is always the main phase. The formation of Y-123 was not observed only in the sample obtained from oxide (BY1), which gives binary mixed oxides. The list of impurities present in each sample after sinterization, obtained by XRD patterns for samples from different preparation procedures, is reported in table 2.

XRD investigation shows that mixing with a mortar is not satisfactory to obtain an intimate mixture; in fact, for the sample BY1 only binary oxides and traces of starting oxides are obtained. In all other cases, the samples are nearly single-phase. In fact if impurities are present, their amount is very low as shown in the XRD spectra. From XRD measurements the lattice parameters of the Y-123 phase, present in a different sample, are obtained and they are listed in table 3. The oxygen content was obtained by standard iodometric titration [11]. For all samples, the oxygen content values show an error of ± 0.2. The *a*-, *b*- and *c*-axes values reported in table 3 show that the samples are orthorhombic.

Table 3. *a*-, *b*-, *c*-axis values obtained from XRD patterns for the Y-123 phase.

Sample	*a*-axis (Å)	*b*-axis (Å)	*c*-axis (Å)	Oxygen content $(7-x)$
BY2	3.812	3.874	11.673	6.70
BY3	3.816	3.880	11.693	6.65
BY4	3.820	3.901	11.698	6.62
BY5	3.846	3.909	11.658	6.74
BY6	3.812	3.884	11.715	6.74
BY7	3.843	3.874	11.627	6.65

Table 4. The sample stoichiometry obtained by EDX measurements. *x*, *y* and *z* values are the atomic ratios in the $Y_wBa_yCu_zO_{7-x}$ formula.

Sample	*w* (Y)	*y* (Ba)	*z* (Cu)
BY2	1.185	2.128	3.095
BY4	1.105	2.136	3.207
BY6	1.097	2.094	2.906
BY7	1.143	2.064	2.936

Figure 2 shows the SEM pictures of the BY3, BY4 and BY6 samples. It can be seen that the surface structure and grain size are different depending on the barium compound used in the starting mixture.

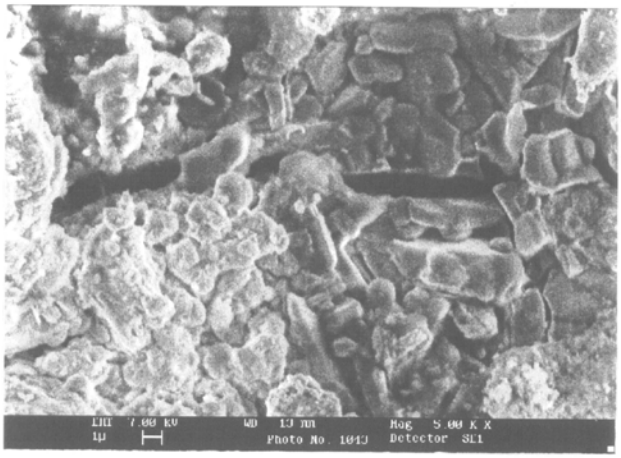
In the BY3 sample (figure 2(*a*)) most of the grains have small size (∼1 μm), in the BY6 sample (figure 2(*c*)) larger grain size (∼10 μm) is observed compared to the BY3 sample and in the BY4 sample (figure 2(*b*)) the grain size has an intermediate value (∼4–5 μm). This indicates that when the starting compounds were used in solution, the grain growth was easier for the intimate mixture between the precursors. The samples were analysed with the EDX in order to obtain the final cation stoichiometry. Only the single-phase Y-123 samples were analysed and the results are reported in table 4. The EDX analyses show that in the cases of peroxide (BY2), nitrate (BY4), neodecanoate (BY6) and autoignition (BY7) process, the final stoichiometry of the samples is nearly Y:Ba:Cu = 1:2:3.

3.1. Optimization of sample preparation

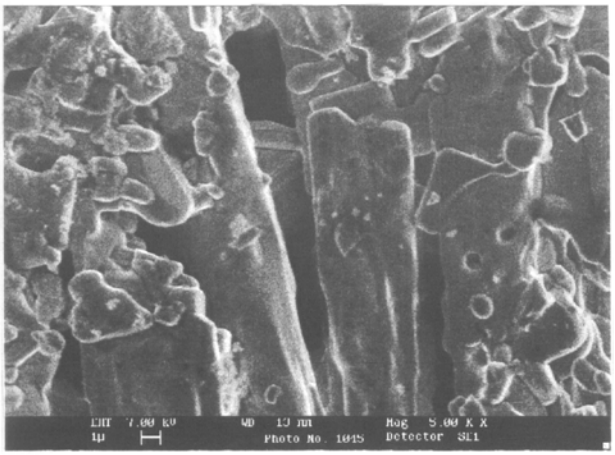
The impurities present in the samples (table 2) obtained with the procedures reported in the experimental section are imputable either to unsatisfactory mixing of precursors or to non-optimal thermal treatments [14]. Therefore, some modifications of sample preparation procedure have been performed with the aim of obtaining Y-123 single-phase samples.

When the sample was prepared starting from oxides, 5–10 ml of nitric acid was added to the mixture of Y, Ba and

(*a*)



(*b*)



(*c*)

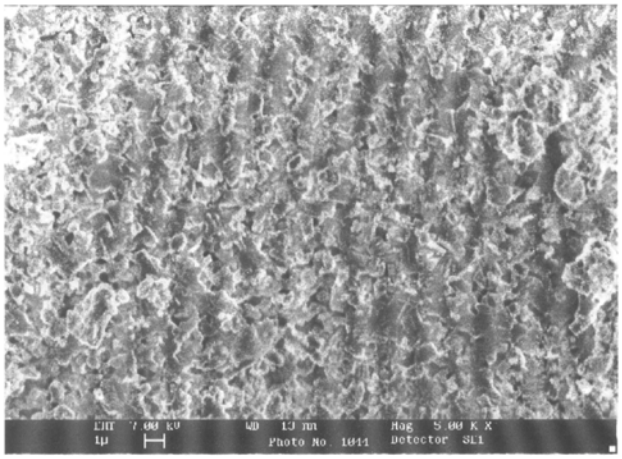


Figure 2. SEM images of (*a*) BY3, (*b*) BY4 and (*c*) BY6 samples.

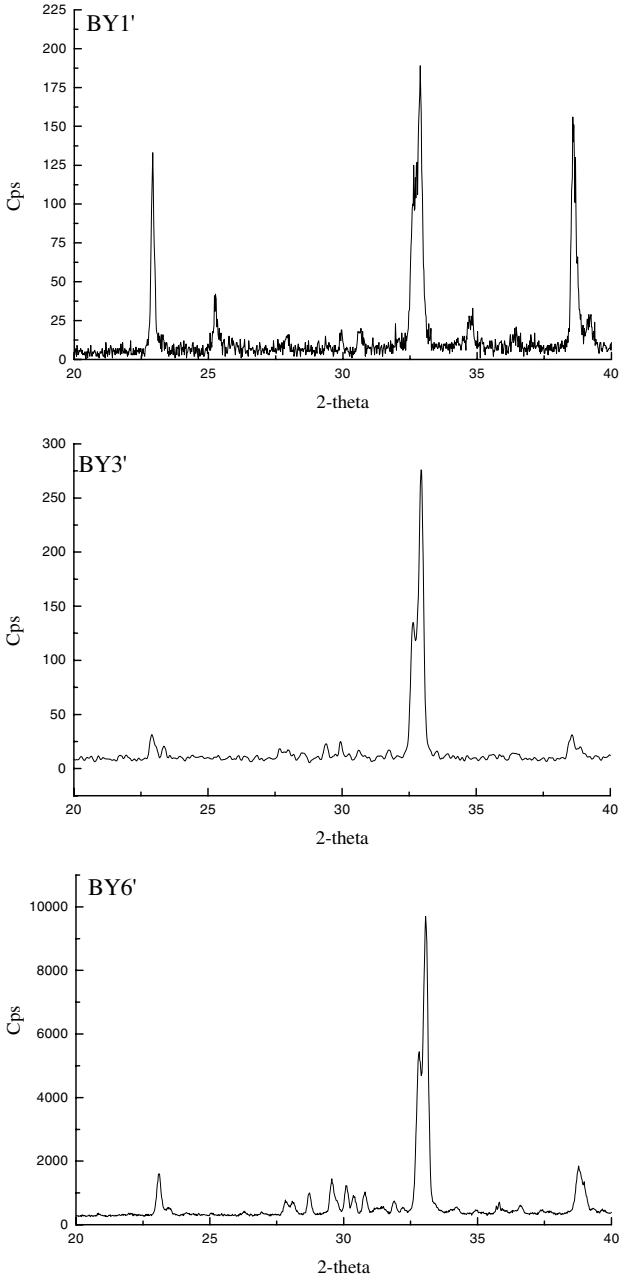


Figure 3. XRD spectra for the samples BY1′, BY3′ and BY6′.

Cu oxides before the grinding in the agate mortar to promote the precursors mixing.

When the YBCO samples were obtained using barium carbonate or acetate, the thermal treatment was modified and a new annealing step, at 900 °C for 8–10 h, was introduced before the other two steps at 920 and 450 °C reported in the experimental section. This allows us to eliminate the impurities which are intermediate compounds deriving from incomplete reactions. When the barium neodecanoate was used, the annealing time for the step at 920 °C was reduced from 5 to 2 h to avoid the Y-211 phase stabilization. In figure 3 the XRD spectra for the samples obtained using oxide, carbonate or neodecanoate (BY1′, BY3′ and BY6′) as barium precursors are shown.

In BY3′ and BY6′ only the signals of Y-123 are present. In the BY1′ sample $BaCO_3$, $BaCuO_2$ and Ba_2CuO_3 ($2\theta \sim 26$ and 34) are still present as minor phases [15].

The above modifications of the sample preparation procedure permit us, independently of the barium precursor used, to obtain the Y-123 single-phase except for the sample

obtained starting from oxides for which Y-123 is however the major phase.

4. Conclusion

YBCO samples were prepared with different barium precursor compounds in order to compare their influence on the final sample characteristics. The YBCO sample preparation was performed using the usual solid-state method [8] and both the simultaneous preparation [9] and autoignition methods (via citrate solution process) [10].

A comparative analysis of the different processes used has been made. The experimental results show that when the thermal treatment reported in the experimental section is used, Ba nitrate as precursor is the best choice for obtaining good quality superconducting samples. Nevertheless, slight modifications of sample preparation procedure allow us to obtain the Y-123 single-phase from all the barium precursors employed.

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